UDC 666.263.2

# STRUCTURAL PARTICULARS AND FORMATION MECHANISMS OF GLASS COATINGS BELONGING TO THE SYSTEM $Na_2O$ – $B_2O_3$ – ZnO – $TiO_2$ – $SiO_2$

L. L. Bragina[1, 2] and O. V. Savvova[1]

Translated from *Steklo i Keramika*, No. 7, pp. 29 – 31, July, 2009.

It is established on the basis of investigations of the particulars of the structure and phase distribution in glasses belonging to the system $Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2$ that spinodal liquation followed by crystallization of rutile with a uniform distribution of the crystalline phase is energetically favored over stable crystallization, which makes it possible to obtain a finely dispersed, silky coating texture with 11 – 12% luster. The composition of the glass matrix is optimized to obtain a mat, glass crystal, coating with high technical – performance and decorative indicators.

***Key words:*** glass coating, crystallization, microliquation, finely dispersed texture, matness, decorativeness.

The current level of knowledge of the glassy state makes it possible to predict, to a large extent, the properties of a material on the basis of its chemical composition. However, this is not true for glass crystal coatings, since these materials are obtained on the basis of the principles of directed crystallization, which promotes the formation of a two- or multiphase structure as a result of heat-treatment of the initial glass [1].

The possibility of changing the phase composition of the glass crystal titanium coatings, the form and content of the crystal phases, the size of the crystals, and other structural characteristics during heat-treatment permits regulating their properties in the required direction. This explains the special attention that is being focused on investigations of the structural particulars and formation mechanisms during the development of lustrous and mat enamel coatings.

The effect of $TiO_2$ can be traced, firstly, with the separation of the melt into two glass phases followed by a metastable liquation process, which gives a finely dispersed volume crystallization of the glass [1]. However, to this day there is no single opinion concerning the role of titanium cations in obtaining complex glasses in which it can be both a glass former and a modifier. It is noted in [2] that the structural role of titanium in glasses as a former of a glass network with tetrahedral coordination and, conversely, as a modifier with octahedral coordination should be analyzed separately in each case, since the Ti – O bonds in an octahedron are of a quite directional character, and the titanium-oxygen octahedra can often be regarded as structural elements of a complex anion.

The possibility of formation of a crystal phase of glass depends on the degree of connectedness of its glass network; invert glasses are more inclined toward crystallization. They include glasses where the molar content of $SiO_2 + B_2O_3$ is ≤ 50%. In studying titanium-containing borosilicate glasses one is drawn to the fact that glass crystal materials can be obtained not only on the basis of invert glasses but also in glasses where the sum of the glass-forming oxides is greater than 50% (molar content). In this case the ratio $TiO_2 : Na_2O < 1$. This condition indicates that excess $TiO_2$ relative to $Na_2O$ in the glass plays an important role in the formation of the glass crystal structure. It should also be noted that the catalyzing effect of $TiO_2$, which results in the appearance of a liquation structure and volume crystallization, first appears in glass compositions where the molar content of $TiO_2$ is greater than a definite minimum value required for obtaining opacified glass enamel coatings (5 – 8%) [2].

Previous investigations [3] have shown that the crystallization capacity of model glasses belonging to the system $Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2$, i.e., additionally containing ZnO as a component that intensifies the crystallization and liquation processes, depends on their thermal history and showed that coatings with different degrees of luster can be obtained by directed crystallization.

The objective of the present work is to establish the structural particulars of and formation mechanism for glass coatings in the indicated system.

[1] National Technical University “Kharkov Polytechnical Institute,” Kharkov, Ukraine.
[2] E-mail: amega@kpi.kharkov.ua.

To do so it was necessary to determine the mechanism of the liquation and crystallization processes in the model glasses under firing conditions. X-ray phase, petrographic, and electron-microscopic methods of analysis, IR spectroscopy, and small-angle x-ray scattering were all used. A photoelectric brightness meter was used to evaluate the luster of the coatings.

The character of the crystallization of the experimental glasses, resulting in the formation of rutile or zinc orthotitanate crystals, depends on the structural parameters of these glasses. The characteristic absorption peak in the IR spectra of such glasses lies in the ranges 650 – 700 and 500 – 600 $cm^{-1}$; its character is distinct and due to the six-fold coordination of titanium [4].

According to the data obtained by IR spectroscopy, in the experimental glasses which lie in the high-silica region of the system chosen, for $TiO_2 : Na_2O > 1$ the absorption peaks observed for the indicated crystals were less sharp than for invert experimental low-silica glasses. This shows that the crystallization power of the glasses decreases with increasing $SiO_2$ content.

We underscore that the zinc present in all titanium-containing model glasses impeded the transition of titanium to four-fold coordination. This is what radically distinguishes them from titanium-containing zinc-free glasses and can be explained by the fact that zinc definitely competes with titanium for incorporation into the glass framework. This is confirmed by the ease with which rutile precipitates in experimental glasses containing titanium, even when the titanium content in them is ≤ 10%[3] $TiO_2$.

The interaction of $TiO_2$ and ZnO in the indicated glasses and glass crystal coatings can be seen also when studying the character of the liquation in them by electron microscopy. We have classified the following groups of the experimental glasses according to the character of the liquation: first group — homogeneous glasses Nos. 14 – 16 with 5% $TiO_2$ content; second group — heterogeneous glasses Nos. 10 – 12 in the bimodal region of liquation with 10% $TiO_2$ content; third group — heterogeneous glasses with 15% $TiO_2$ content (the labeling and compositions of the glasses are presented in [5]). This group of glasses falls into the same region of spinodal liquation that corresponds to the more uniform finely dispersed structure of opacified glasses as compared with glasses which lie in the bimodal region. The glasses in the fourth group with 25% ZnO and 10 – 20% $TiO_2$ are heterogeneous and fall outside the liquation range. The crystal phase in them is characterized by large sizes and nonuniform distribution in the glass matrix. The data obtained are in agreement with the results obtained from investigations of the regions of liquation in the titanium-containing glasses [6].

Small-angle x-ray scattering established that the composition of microliquation regions in spinodal liquation glasses is close to that of the crystalline compounds which are found in these glasses. Consequently, spinodal liquation followed by crystallization is energetically more favorable for obtaining mat, glass crystal coatings than stable crystallization. The group-III glasses with 15 – 20% $TiO_2$ are recognized as being more promising.

The difference of the mechanisms of nucleation of the crystalline phase at the initial stages in group-III and -IV glasses is due to, first and foremost, the coordination state of boron. According to IR spectroscopy data, the boron in group-IV glasses (Nos. 4, 9, 13) is mainly in four-fold coordination, which, as is well known, strengthens the structure of the network. This explains the fact that the first crystalline phase appears only at temperature 700 – 780°C; this is confirmed by XPA data on the presence of peaks of the crystalline phase in the corresponding x-ray diffraction patterns, whose character attests to the crystalline nature of the microinhomogeneities.

Glasses in the spinodal region (Nos. 1 – 3, 8) are characterized by the fact that the groups $[BO_3]^{3-}$ and $[BO_4]^{4-}$ are present simultaneously, and for $Na_2O : TiO_2 = 1$ (glasses Nos. 5 – 7) the presence of boron in three-fold coordination is the predominant factor. For glasses in this group the formation of the first crystalline phase ($Na_xTiO_2$) is recorded already at 600 – 630°C, indicating more intense crystallization of such glasses at relatively low temperatures.

The results of the petrographic and polythermal analyses as well as XPA and electron microscopy showed that a coarsely dispersed texture of glass coatings with 2.4 μm high surface asperities and brightness 9 – 10% can be obtained in coatings based on the glasses Nos. 4, 9, and 13, where $TiO_2 : ZnO = 1.0$, 0.4, and 0.6. This is due to the fact that intense crystallization of willemite with 90 – 120 μm grains in amounts of 15 – 20% and zinc orthotitanate with 1 – 4 μm grains in amounts 5% prevails. For $TiO_2 : ZnO = 1.0$ and 1.33 rutile is observed to crystallize predominately in the glasses Nos. 3, 7, and 8 with a more uniform distribution of the crystalline phase in the amounts 15 – 20% and grain size 30 – 60 μm. It is possible to obtain coatings with a finely dispersed, silky texture with brightness 11 – 12%.

The composition of the glass matrix for obtaining an MP-8 mat, glass crystal coating with high technical – performance (microhardness — 4250 MPa, chemical stability — class A) and decorative indicators: brightness — 11%, roughness — 2.35 μm with firing at temperature 830°C for 2 – 3 min (Ukraine Patent No. 52075A) was optimized on the basis of the investigations performed. Experimental prototype tests of an MP-8 mat coating were performed under the conditions at "Émal'zavod" JSC (Khar'kov). The results confirmed that it effectively protects architectural – construction articles.

In summary, investigations of the structural particulars and phase distribution in glasses in the system $Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2$ have established that spinodal liquation followed by crystallization is energetically more advantageous than stable crystallization. The required matness of the coatings and height of surface asperities ranging from 1.5 to

[3] Here and below — content by weight.

2.0 μm and, as a result, a uniform (“satin”) surface of the coating are obtained for ($SiO_2 + B_2O_3$ ) content > 50 parts by weight and ratios $Na_2O : TiO_2 \leq 1$.

## REFERENCES

1. P. D. Sarkisov, *Directed Crystallization of Glass — The Basis for Obtaining Multifunctional Glass Crystal Materials* [in Russian], D. I Mendeleev Russian Chemical Technology University, Moscow (1997).
2. R. Ya. Khodakovskaya, *Chemistry of Titanium-Containing Glasses and Enamels* [in Russian], Khimiya, Moscow (1978).
3. L. Bragina, G. Voronov, O. Savova, and N. Sobol, “Ground enamels based on technogenius raw material basis and matte enamels for architectural-building purposes,” in: *Innovative Trends in Enamelling Technology*, Ostrava (2004), pp. 20 – 25.
4. A. N. Lazarev, *Vibrational Spectra and the Structure of Silicates* [in Russian], Nauka, Leningrad (1968).
5. L. L. Bragina and O. V. Savvova, “Glass crystal matted coatings in the system $Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2$,” *Steklo Keram.*, No. 8, 22 – 25 (2008).
6. B. G. Bragina (ed.), *Two-Phase Glasses: Structure, Properties, and Applications* [in Russian], Nauka, Moscow (1991).